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# Effect of nuclear motion on the critical nuclear charge for two-electron atoms

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A variational method for calculating the critical nuclear charge  $Z_C$  required for the binding of a nucleus to two electrons is reported. The method is very effective and performs well compared to the traditional variational principle for calculating energy. The critical nuclear charge, which corresponds to the minimum charge required for the atomic system to have at least one bound state, has been calculated for heliumlike systems with both infinite and finite nuclear masses. The value of  $Z_C = 0.911\,028\,2(3)$  is in very good agreement with recent values in the literature for two-electron atoms with an infinite nuclear mass. When nuclear motion is considered, the value for  $Z_C$  varies from  $0.911\,030\,3(2)$  for that with a nuclear mass of Ne (the largest heliogenic system considered) to  $0.921\,802\,4(4)$  for a system with the nuclear mass of a positron. In all cases the energy varies smoothly as  $Z \rightarrow 0$ . It is found that for the finite nuclear mass case, in agreement with previous work for the fixed nucleus mass system, the outer electron remains localized near the nucleus at  $Z = Z_C$ . Additionally, the electron probability distribution is calculated to determine the behavior of the electrons at low  $Z$ .

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## I. INTRODUCTION

There are two key physical factors influencing the stability of atoms and molecules with a fixed number of particles, interacting via Coulomb interactions: the mass and charge of the particles. The quantum-mechanical three-body system with Coulomb interaction is ideal for an in-depth investigation into these fundamental factors due to the feasibility of high-accuracy calculations that include the nonadiabatic and correlation effects associated with the particle motion. Recently, we considered explicitly the role of mass. An exact stability boundary for unit-charge three-body systems as a function of the particle masses was determined, demonstrating the important role that mass-symmetry breaking plays in the instability of Coulomb three-body systems [1,2]. In the present work we investigate the role that charge plays in the stability of two-electron atoms and ions. The critical nuclear charge  $Z_C$  for which the three-body system remains stable for both the infinite nuclear mass system  $Z_C(\infty)$  and the finite nuclear mass system  $Z_C(\text{finite})$  for a wide range of nuclear masses is determined. Several authors have investigated the infinite nuclear mass case. Very recently, Estienne *et al.* [3] calculated a definitive value for  $Z_C(\infty)$ , confirmed by Pilón and Turbinder [4], resolving recent contradictions in the literature [5,6]. Estienne *et al.* [3] calculated  $Z_C(\infty) = 0.911\,028\,224\,077\,255\,73(4)$  using high-precision variational calculations in Hylleraas coordinates with double and triple basis sets to quadruple precision and explored the electronic structure and behavior of the outer electron as  $Z \rightarrow Z_C$ . In this paper, high-accuracy nonrelativistic ground-state energies and wave functions of a range of two-electron systems will be determined using a method in which the quantum effects of nuclear motion and electron correlation are included from the outset. We first determine the critical nuclear charge for a system with infinite nuclear mass, demonstrating excellent agreement with the recent literature value [3], and then calculate the critical nuclear charge for several finite nuclear mass systems to establish the effect of nuclear motion on the

critical nuclear charge. Various bound-state properties of the critical nuclear charge system are calculated and compared to those calculated for helium and the hydride ion.

## II. VARIATIONAL PRINCIPLE FOR THE THRESHOLD VALUE OF NUCLEAR CHARGE

A variational method, analogous to that used for the direct calculation of the threshold mass [2,7], is formulated for the direct determination of the threshold (or critical) nuclear charge. Based on the variational principle for the generalized eigenvalue problem, Rebane and Kuzminskii [7] showed that the lowest eigenvalue  $\lambda_0$  corresponds to  $\min K(\phi)$  where

$$K(\phi) = \frac{\int \phi \hat{P} \phi dV}{\int \phi \hat{Q} \phi dV}. \quad (1)$$

Here  $\hat{P}$  is a self-consistent operator bounded from below and  $\hat{Q}$  is a positive-definite, self-conjugate operator [7]. The eigenvalues  $\lambda_j$  are the extremals of  $K$ , satisfying the equation

$$\hat{P} \psi_j = \lambda_j \hat{Q} \psi_j, \quad j = 0, 1, 2, \dots, \quad (2)$$

which arises from the requirement that the first variation vanishes, i.e.,  $\delta K \equiv 0$  [7].

This algorithm can be applied to the calculation of the threshold value of the nuclear charge. The Schrödinger equation in atomic units for a two-electron atom of the form  $e^-e^-M^{Z+}$ , where  $M$  is the mass of the nucleus and  $Z$  is the nuclear charge, is

$$\left( -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{1}{2M} \nabla_3^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_3} \right) \psi = E \psi, \quad (3)$$

where  $r_1$  and  $r_2$  are the distances of the first and second electrons from the nucleus, respectively, and  $r_3$ , usually referred to as  $r_{12}$ , is their mutual separation. A scaling of the coordinates  $r_i$  by  $Z$  results in the following  $Z$ -scaled Schrödinger equation:

$$\left( -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{1}{2M} \nabla_3^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{Z r_3} \right) \psi = \frac{E}{Z^2} \psi. \quad (4)$$

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At the stability threshold (the beginning of the essential spectrum of the operator), the wave function satisfies (4) with  $E \equiv E_{\text{th}} = -Z^2 M/2(1+M)$ , where  $E_{\text{th}}$  is simply the ground-state energy of the hydrogenlike electron-nucleus two-particle system that corresponds to the energy of the lowest dissociation threshold, which in this case is electron detachment. Therefore,

$$\left(-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{2M}\nabla_3^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{Z} \frac{1}{r_3}\right)\psi = \frac{E_{\text{th}}}{Z^2}\psi. \quad (5)$$

A rearranged Eq. (5) is a particular case of (2), where the operators  $\hat{P}$  and  $\hat{Q}$  are defined as

$$\hat{P} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{2M}\nabla_3^2 - \frac{1}{r_1} - \frac{1}{r_2} + M/2(1+M), \quad (6)$$

$$\hat{Q} = \frac{1}{r_3} \quad (7)$$

such that

$$\hat{P}\psi = \lambda_0 \hat{Q}\psi. \quad (8)$$

These definitions of the operators satisfy the requirement that  $\hat{P}$  is bounded from below (cf. the standard assumption that the Hamiltonian operator is bounded below in the variational principle [8]) and that  $\hat{Q}$  is a positive-definite self-conjugate operator [7]. The eigenvalue  $\lambda_0$  corresponds to the threshold charge of the nucleus, i.e.,

$$\lambda_0 = -\frac{1}{Z_C}. \quad (9)$$

The value of  $Z_C$  corresponds to the nuclear charge for which the system is still stable. In the limit when the trial wave function tends to the exact solution of (8) this value tends to the exact value of the critical nuclear charge  $Z_C$ .

### III. METHOD

The generalized eigenvalue equation (8) with the operators defined in (6) and (7) is the starting point for the solution of the singlet ground state of two-electron atoms and ions of the form  $e^-e^-M^{Z+}$ , where  $M$  is the mass of the nucleus and  $Z (= Z_C)$  is the critical nuclear charge for binding. The center-of-mass motion is separated off and the problem is recast in perimetric coordinates defined as  $z_i = r_j + r_k - r_i$ , where  $i, j$ , and  $k$  denote cyclic permutation of 1, 2, and 3. The resulting generalized eigenvalue equation is solved using a series solution method described by Cox *et al.* [9,10] by expanding the wave function in a triple orthogonal set of Laguerre functions [11] in scaled perimetric coordinates

$$\psi(z_1, z_2, z_3) = e^{-(\alpha z_1 + \beta z_2 + \gamma z_3)/2} \times \sum_{l,m,n=0}^{\infty} A(l,m,n) L_l(\alpha z_1) L_m(\beta z_2) L_n(\gamma z_3), \quad (10)$$

where  $L_n(x)$  is the Laguerre polynomial of degree  $n$  and  $\alpha$ ,  $\beta$ , and  $\gamma$  are nonlinear variation parameters. This results in

a 57-term recursion relation between the coefficients, which is used to form a sparse secular determinant that is solved in truncated form to give the eigenvalues as a function of basis set size  $N$ . For the singlet ground state, the spatial function must be symmetric to exchange of the electrons, therefore the wave function takes the form

$$\psi(z_1, z_2, z_3) = e^{-(\alpha z_1 + \beta z_2 + \gamma z_3)/2} \times \sum_{l,m,n} A(l,m,n) [L_l(\alpha z_1) L_m(\beta z_2) L_n(\gamma z_3) + L_l(\alpha z_2) L_m(\beta z_1) L_n(\gamma z_3)]. \quad (11)$$

In this work determinants of order 1078, 2856, and 4389 are considered, which correspond to wave functions represented by complete polynomials of order  $\omega = 21, 30$ , and 35, respectively, in the scaled perimetric coordinates, where  $\omega = l + m + n$  and the numbering takes advantage of the preserved symmetry [9,11]. The constraint  $\alpha = \beta$  is imposed to take advantage of the quasiorthogonal character of the wave function, but  $\gamma$  is allowed to vary independently to allow for an explicit dependence on  $r_{12} (= r_3)$  in the exponential behavior at large  $r$ , which may be important at noninteger low  $Z$ . When  $\gamma = \alpha + \beta = 2\alpha$  the exponent in the wave function models, in principle, the correct asymptotic behavior of the solution of the Schrödinger equation for two-electron atoms at large  $r_1$  and  $r_2$  [12] (for an English translation of [12] see [13]).

The nonlinear variational parameters  $(\alpha, \gamma)$  were optimized using the bound optimization by quadratic approximation algorithm [14]. All optimizations were performed in double precision (16 digits) for systems that are converged to less than 12 significant figures, but it was necessary to use quadruple precision (32 digits) for higher levels of convergence and for the accurate calculation of all the expectation values involving Dirac delta functions discussed in Sec. IV. The particle-electron mass ratio for the helium nucleus (taken as the  $\alpha$  particle), proton, muon, and tauon were taken directly from the latest set of recommended values by the Committee on Data for Science and Technology (CODATA) [15]. For  $Z \geq 3$  the experimental atomic masses  $M$  (u) for the most abundant isotope with  $Z \geq 3$  were taken from Ref. [16] and converted to atomic units via the relationship  $M$  (a.u.) =  $M$  (u)  $\times m_u/m_e$ . The value of the unified atomic mass constant is  $m_u = 1.660\,538\,921(73) \times 10^{-27}$  kg and the mass of the electron  $m_e = 9.109\,382\,91(40) \times 10^{-31}$  kg [15]. The nuclear masses in atomic units were then obtained by removing the appropriate number of electrons and are provided in Table I. All the systems listed in Table I are stable in their ground state and can be used as initial systems to determine the boundary of stability for each system of a given mass  $M$  as the charge  $Z$  decreases. Note that due to the mass scaling rule these results also determine analogous systems with the same particle-mass ratios.

### IV. RESULTS AND DISCUSSION

#### A. Energy as a function of nuclear charge $Z$

The calculated energies for the helium atom and its isoelectronic ions, for both the infinite nuclear mass and finite nuclear mass systems, are in excellent agreement with the most recent high-accuracy values reported in the literature [17,18]. The energy values calculated in this work, using the series

TABLE I. Bound on the critical nuclear charge  $Z_C$  for two-electron systems, calculated using a 2856-term basis with two nonlinear variational parameters; the digit given in parentheses is not considered converged. The nuclear mass data  $M$  (in a.u.) for the muon, tauon, and helium and its isoelectronic ions  $Z = 1$ –10 is also provided.

Initial system	Nuclear mass $M$	$Z_C$
$e^-e^-e^+$	1	0.921 802 4(4)
$e^-e^-\mu^+$	206.768 2843	0.911 392 7(8)
$e^-e^-\tau^+$	3477.15	0.911 050 1(6)
$^1\text{H}^- (e^-e^-p^+)$	1836.152 672 45	0.911 069 7(3)
$^4\text{He}$	7294.299 536 1	0.911 038 6(9)
$^7\text{Li}^+$	12 786.3918	0.911 034 2(0)
$^9\text{Be}^{2+}$	16 424.2047	0.911 032 8(8)
$^{11}\text{B}^{3+}$	20 063.7360	0.911 032 0(3)
$^{12}\text{C}^{4+}$	21 868.661 82	0.911 031 7(2)
$^{14}\text{N}^{5+}$	25 519.0423	0.911 031 2(2)
$^{16}\text{O}^{6+}$	29 148.9456	0.911 030 8(5)
$^{19}\text{F}^{7+}$	34 622.9703	0.911 030 4(3)
$^{20}\text{Ne}^{8+}$	36 433.9889	0.911 030 3(2)
$^\infty\text{H}^-$	$\infty$	0.911 028 2(3)

solution method described above with a 2856-term wave function, are accurate to at least 13 significant figures (s.f.) for the infinite nuclear mass systems (except  $\text{H}^-$ , which is converged to 11 s.f.) and to at least 11 s.f. for the finite nuclear mass systems. It is worth noting that the agreement between the finite masses used here and those in the literature is no greater than 8 s.f. for  $Z \geq 3$ . The energies for systems with the nucleus in motion are less negative than those with fixed nucleus. The energy difference is of the order of  $10^{-4}$  a.u. for  $\text{H}^-$  to  $\text{Be}^{2+}$  and  $10^{-3}$  a.u. for  $\text{B}^{3+}$  to  $\text{Ne}^{8+}$  and so increases from less than  $1 \text{ kJ mol}^{-1}$  to about  $7 \text{ kJ mol}^{-1}$ . However, the effect of nuclear motion on the total energy of the system becomes smaller as the nuclear mass increases, as expected.

In Fig. 1, the energy of the ground state of two-electron atoms, corresponding to the two-electron Hamiltonian with  $M = \infty$ , is shown for a range of integer and noninteger values

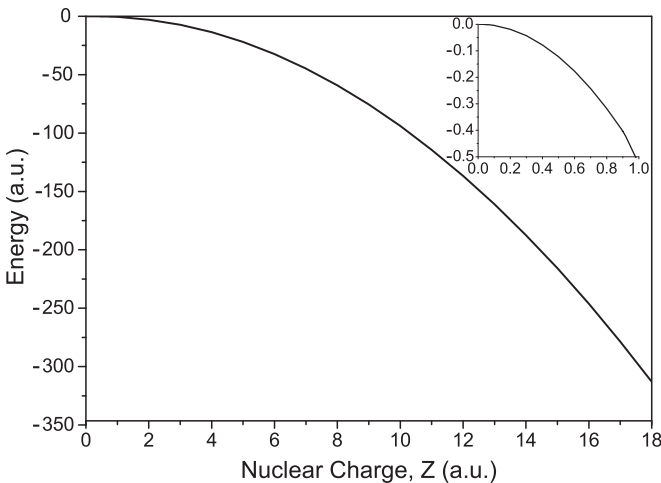


FIG. 1. Ground-state energy of  $e^-e^-M^{Z+}$ , with mass  $M = \infty$ , as a function of  $Z$ .

of  $Z$ . A general theorem exists stating that the energy is a concave function of any parameter entering the Hamiltonian linearly [19]. The ground-state energy is therefore a concave function of the charge  $Z$  (and also the inverse mass  $M^{-1}$  when  $M$  is finite). It is clear from Fig. 1 that, as expected, the energy continues to be a continuous function of  $Z$  for noninteger low- $Z$  values.

## B. Critical charge $Z_C$ required for binding

The critical nuclear charge required for binding was determined using the variational method described above with a range of nuclear masses from 1 to infinity (see Table I). Additionally, to check this method, the total energy for each  $e^-e^-M^{Z+}$  system was calculated using the standard Hamiltonian in (3) and compared with the threshold energy  $E_{\text{th}}(1, M) = -Z^2 M / 2(1 + M)$  for that particular  $Z$  to determine if the three-body system remained bound. Given that the variational energy calculations provide an upper bound to the true energy, the smallest value of  $Z$  for which the calculated energy lies below the electron detachment threshold is an upper bound to the exact value of the critical charge  $Z_C$ . Similarly, the variational method for the direct determination of  $Z$  described in Sec. II provides an upper bound. Convergence behavior was determined by evaluating the energy and critical  $Z$  as a function of basis set size. The convergence of  $Z$  near the boundary of stability was slower than the energy convergence (Table II). It was found that both methods, the variational method for the direct determination for  $Z_C$  and the energy comparison method, provided the same value for  $Z_C$  to the reported accuracy for a given basis set size but the present method provided the value in a single calculation, reducing the computational effort significantly.

Using the series solution method with a 2856-term wave function, it is found that  $Z_C = 0.911 028 2$ , which is in excellent agreement with the most recent literature value of  $Z_C = 0.911 028 224 077 255 73(4)$  using a multiple basis set method with up to 2276 terms [3]. Additional converged digits are obtained by going to larger basis set sizes (Table II). Additionally, the results presented here using a Laguerre-based single basis set method further support the results obtained by Estienne *et al.* [3] regarding the contradictory values in the literature.

The minimum (critical) charge of the third particle or nucleus required to bind two electrons is given in Table I starting from the stable systems  $e^-e^-M^{Z+}$  with finite nuclear masses  $M$  ranging from the mass of a positron equal to 1 to the

TABLE II. Rate of convergence with basis set size (number of basis functions  $N$  at order  $\omega$ ). Converged digits are bold. The energy convergence of the helium atom is compared with the charge convergence for  $Z_C$ ; the values of  $E(^{\infty}\text{He})$  and  $Z_C(^{\infty})$  are given in a.u. In both cases, the nuclear mass is taken as infinite.

Dimension $\omega$	Number of terms $N$	$E(^{\infty}\text{He})$	$Z_C(^{\infty})$
21	1078	<b>-2.903 724 377 026 604</b>	<b>0.911 028 431 8</b>
30	2856	<b>-2.903 724 377 034 010</b>	<b>0.911 028 235 5</b>
35	4389	<b>-2.903 724 377 034 099</b>	<b>0.911 028 227 1</b>
45	8924		<b>0.911 028 224 4</b>

mass of a neon nucleus equal to 36 433.9889. Rebane [20] has calculated the regions of unconditional stability and instability of Coulomb systems with varying particle charges for fixed ratios of the particles masses and reports values starting from  $\text{Ps}^-$  and  $\text{Mu}^-$  of 0.9296 and 0.9174, respectively. The results in Table I for these systems improve on these upper bounds (0.921 802 4 and 0.911 392 7, respectively) and are highly accurate. Furthermore, here the upper bound on the critical value of the charge has been reported for a range of systems with heliogenic nuclear masses. The data reveal that as the mass decreases a greater nuclear charge is required to ensure binding. The difference in nuclear charge for the helium isoelectronic sequence is of the order of  $4 \times 10^{-5}$ , but as the mass is reduced from that of a proton to that of a positron, the difference in the critical charge for binding is much greater at  $1 \times 10^{-2}$ . This is attributed to the increased nuclear motion of a light particle requiring a greater attractive nucleus-electron interaction to trap the second electron and overcome the electron-electron repulsion.

### C. Bound-state properties as a function of nuclear charge $Z$

To determine the quality of the solutions obtained, various expectation values have been calculated with the best 2856-term wave function optimized using 32-digit precision in each case. The properties presented in Table III include the expectation values of the interparticle distances  $r_i$  and various powers  $r_i^{-1}$  and  $r_i^2$ , the two-particle Dirac delta functions  $\delta(r_i)$ , and the two-particle cusps  $v_i$ . In this table, the subscript 1 refers to the nucleus-electron interaction and the subscript 3 refers to the electron-electron interaction. The extent to which the virial condition  $\langle \hat{V} \rangle = -2\langle \hat{T} \rangle$  is satisfied also provides a measure of the quality of the solution. It was found that for all systems, including at  $Z_C$ , the factor  $\eta$  defined as

$$\eta = \left| \frac{\langle \hat{V} \rangle}{\langle \hat{T} \rangle} + 2 \right|, \quad (12)$$

TABLE III. Expectation values  $\langle X_i \rangle$  (in a.u.) of some bound-state properties for the ground states of He,  $\text{H}^-$ , and  $Z_C$ . The He and  $\text{H}^-$  data are reported to known accuracy (where the digit in parentheses is not converged) by comparison with literature [21,22] to gauge the accuracy of the values at  $Z_C$ . The subscripts 1 and 3 designate the nucleus-electron and electron-electron interactions, respectively. Data were calculated using a matrix size of 2856. For comparison, the  $Z_C$  values obtaining using the standard Hamiltonian in (3), rather than the  $Z$ -scaled Hamiltonian in (4), are reported.

Property	$^\infty\text{He}$	$^\infty\text{H}^-$	$^\infty Z_C = 0.911\,028\,2(3)$	$^4\text{He}$	$^4 Z_C = 0.911\,038\,6(9)$
$\langle r_1 \rangle$	0.929 472 294 87(2)	2.710 178 27(3)	4.146 663	0.929 607 915 01(1)	4.147 455
$\langle r_3 \rangle$	1.422 070 255 56(3)	4.412 694 4(8)	7.082 812	1.422 247 512 60(4)	7.084 170
$\langle r_1^{-1} \rangle$	1.688 316 800 717 0(6)	0.683 261 767 6(8)	0.578 109	1.688 076 584 669 6(5)	0.578 030
$\langle r_3^{-1} \rangle$	0.945 818 448(8)	0.311 021 502 2(9)	0.223 37(5)	0.945 697 223 219(7)	0.223 338
$\langle r_1^2 \rangle$	1.193 482 995 0(0)	11.913 699(4)	39.745 474	1.193 834 894 4(0)	39.762 659
$\langle r_3^2 \rangle$	2.516 439 312 8(0)	25.202 02(4)	81.234 424	2.517 061 842 4(5)	81.268 355
$\langle \delta(r_1) \rangle$	1.810 429(2)	0.164 552 8(7)	0.119 094	1.809 672 4(1)	0.119 049
$\langle \delta(r_3) \rangle$	0.106 345 3(9)	0.002 73(8)	0.001 115	0.106 299 9(8)	0.001 114
$\eta$	$1.8 \times 10^{-20}$	$2.4 \times 10^{-20}$	$9.4 \times 10^{-20}$	$4.6 \times 10^{-22}$	$1.4 \times 10^{-20}$
$v_1^a$	-1.999 999 1	-0.999 999 97	-0.910 987	-1.999 725 0	-0.910 873
$v_3^b$	0.499 987 0	0.499 886 5	0.497 802 5	0.499 987 1	0.497 802 2

<sup>a</sup>The exact value of  $v_1$  for the infinite nuclear mass systems is  $-Z$ . For  $^4\text{He}$  and  $^4 Z_C$  the exact values to nine decimal places are  $-1.999\,725\,850$  and  $-0.910\,913\,812$ , respectively.

<sup>b</sup>The exact value of  $v_3$  is 0.5.

where  $\langle \hat{V} \rangle$  and  $\langle \hat{T} \rangle$  are the expectation values of the potential and kinetic energy, respectively, was calculated to be less than  $9.5 \times 10^{-20}$ , which is close to the exact value of zero.

Expectation values of the interparticle coordinates for the systems considered in Table I are in very good agreement with the values reported by Frolov [21,22] for the helium isoelectronic sequence; the He and  $\text{H}^-$  values are provided in Table III. To judge the quality of the wave function at noninteger  $Z$  the value of  $\langle r_3^{-1} \rangle$  at  $Z_C$  was compared with that reported in the literature for the infinite nuclear mass system. Estienne *et al.* [3] used the Hellman-Feynman theorem

$$\frac{dE}{d(1/Z)} = \int \psi^* \frac{\partial \hat{H}}{\partial (1/Z)} \psi dv = \left\langle \frac{1}{r_3} \right\rangle, \quad (13)$$

where  $\hat{H}$  is the Hamiltonian of the system and  $\psi$  the wave function, to confirm the accuracy of their value calculated as the slope of a linear extrapolation of infinite nuclear mass energy against reciprocal nuclear charge  $Z$ . In this work, the calculated value of  $\langle r_3^{-1} \rangle$  at  $Z_C$  using the  $Z$ -scaled Hamiltonian is 0.2451(9), which agrees well with their reported value of 0.245 189 063 9(1). However, it should be noted that using the wave function corresponding to the standard Hamiltonian in (3) for a two electron atom or ion, rather than the  $Z$ -scaled Hamiltonian in (4), yields a value of  $\langle r_3^{-1} \rangle = 0.223\,37(5)$ , i.e., the expectation value reported previously needs to be unscaled to compare with an expectation value calculated using a wave function obtained from a direct energy calculation using (3) at  $Z = Z_C$ .

The two-body cusp ratios were determined using [22,23]

$$v_i = \langle \hat{v}_i \rangle = \frac{\langle \delta(r_i) (\partial / \partial r_i) \rangle}{\langle \delta(r_i) \rangle}. \quad (14)$$

The exact value of  $v_1$ , the nucleus-electron cusp, is  $-\frac{ZM}{1+M}$ , which reduces to  $-Z$  for the infinite nuclear mass systems, and the exact value of  $v_3$ , the electron-electron cusp, is 0.5. The values in Table III indicate that the cusp values at  $Z_C$  are



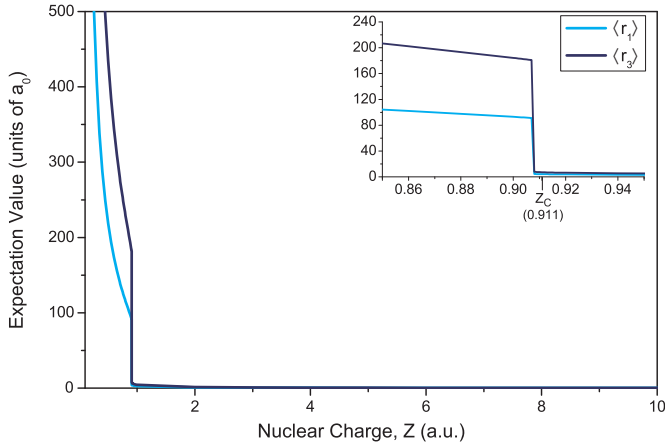


FIG. 2. (Color online) Expectation values  $\langle r_1 \rangle$  and  $\langle r_3 \rangle$  with  $M = m_p = 1836.152\,672\,45$ , as a function of nuclear charge  $Z$ . The critical nuclear charge  $Z_C$  is labeled in the inset. This figure is representative for all  $M \geq m_p$ .

not quite as good as those for helium and the hydride ion, but are quite reasonable.

Expectation values of the interparticle coordinates  $\langle r_1 \rangle$  and  $\langle r_3 \rangle$  as a function of nuclear charge  $Z$  are shown in Fig. 2. There is no appreciable difference between the figure for mass  $M = \infty$  and when taking the finite mass equal to that of a proton, i.e.,  $M = 1836.152\,672\,45$ , as the values differ only in the fourth or fifth significant figure, therefore only the latter is shown. For  $Z < 1$  (see inset of Fig. 2), the electrons appear to remain weakly bound to just below  $Z_C$  and then there is an abrupt jump to large values of  $\langle r_i \rangle$  as the nuclear charge is no longer sufficient to bind the electrons; no such jump is observed in the total energy (Fig. 1) at this point. Figure 2 indicates that close to  $Z_C$  (i.e., at  $Z \approx 0.910$ ) the electrons remain localized, even though the total energy is above the lowest continuum threshold. This behavior is independent of the nuclear motion. Complete electron detachment occurs at  $Z < 0.910$ . It is

not clear in the present work whether this is a physical phenomenon or an artifact. Estienne *et al.* [3] observed that their nonlinear parameter describing the asymptotic behavior of the outer electron does not tend to zero as  $Z \rightarrow Z_C$  as would happen if the outer electron would move to infinity at the critical point. They attributed localization of the wave function at a finite distance from the nucleus below the critical point to the existence of resonances induced by the shape of the atomic potential.

To further elucidate the electronic structure near the critical nuclear charge, the probability distribution for the electron-nucleus distance  $r_1$  ( $= r_2$ ) and for the electron-electron distance  $r_3$  have been calculated using

$$\langle \delta(r_i - r) \rangle = \iiint \psi(r_1, r_2, r_3) \delta(r_i - r) \psi(r_1, r_2, r_3) dr_1 dr_2 dr_3. \quad (15)$$

The probability distribution for the helium atom ( $Z = 2$ ) is compared to that of the hydride ion ( $Z = 1$ ) and the critical nuclear charge system ( $Z = Z_C$ ) (Fig. 3). Again, there is no discernible difference between the data for the infinite nuclear mass systems and those for the finite nuclear mass systems, where the nuclear mass at  $Z_C$  is taken as the proton mass. This is because changes due to nuclear motion appear in the fourth significant figure. The nucleus-electron probability density, often referred to as the single-particle density, and the electron-electron probability density, often referred to as the intracule density, show that all three systems have the same basic profile. The expected cusp condition of the nucleus-electron probability distribution is much less pronounced in the anionic systems, due to the reduced nuclear charge. A maximum occurs in the electron-electron distribution for all three systems, but the density is greatly diminished and the maximum shifts to greater electron-electron separation for the anionic systems. Furthermore, as the charge decreases the probability distribution goes to zero much more slowly. It is clear from these figures that the excess negative charge dominates the interactions, resulting in the electron density

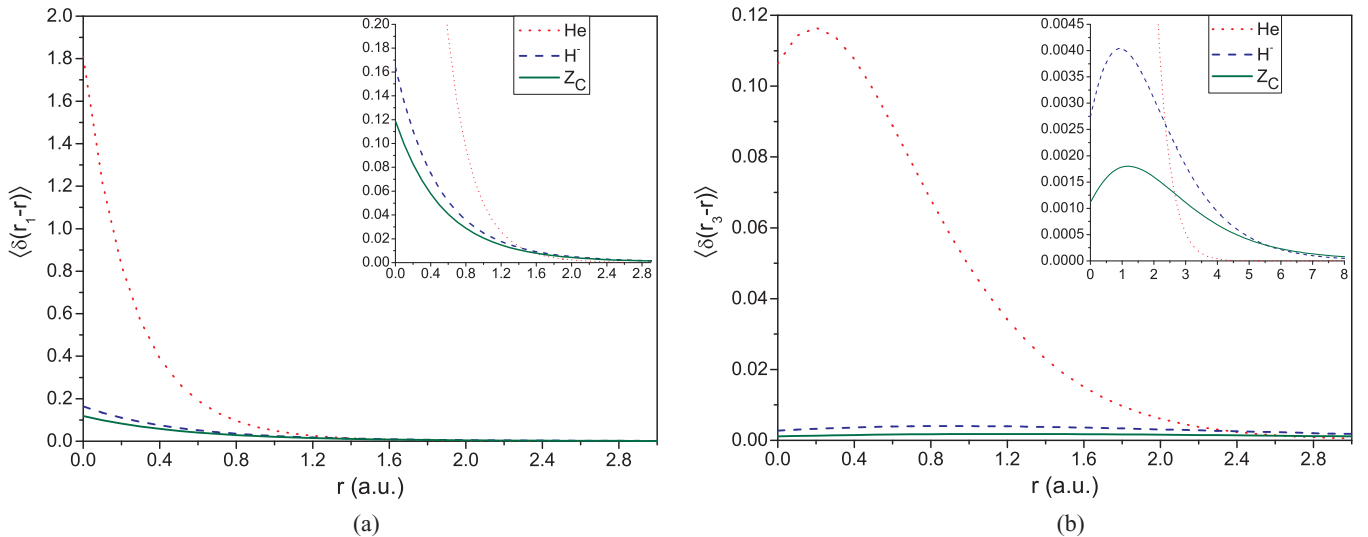


FIG. 3. (Color online) Probability distributions calculated using (a)  $\langle \delta(r_1 - r) \rangle$  and (b)  $\langle \delta(r_3 - r) \rangle$ , for  ${}^4\text{He}$  ( $Z = 2$ ),  ${}^1\text{H}^-$  ( $Z = 1$ ), and  $Z_C$  for the finite nuclear mass systems where  $M = m_p = 1836.152\,672\,45$  for  $Z_C$ . These figures are indistinguishable from those with  $M = \infty$ .

becoming more diffuse, diminishing electron density close to the nucleus.

## V. CONCLUSION

A variational method for the direct calculation of the stability threshold to electron detachment has been introduced and proven to be very effective compared to standard methods. The minimum charge required for binding of two electrons has been calculated both with (i) infinite nuclear mass and (ii) explicit consideration of nuclear motion with a range of finite nuclear masses. Taking account of the relative motion of all the particles in the system and the nonadiabaticity and correlation effects associated with this motion changes  $Z_C$  by at most  $4 \times 10^{-5}$  for the heliogenic mass systems, but becomes more significant,  $1 \times 10^{-2}$ , when the masses are reduced to those of exotic particles such as positrons. Furthermore, very quickly the nuclear charge becomes insufficient to hold a bound state.

The  $Z_C(\infty)$  and  $Z_C(\text{finite})$  for heliogenic nuclear masses agree to four significant figures and take the value of 0.9110, which is very close to the nuclear charge of 1 in the real system  $\text{H}^-$ . Particularly interesting is that the energy remains smooth and continuous as  $Z \rightarrow 0$ , but the expectation values of the interparticle coordinates in the system contain a jump to large distance as the nuclear charge goes through the critical point and the electron detaches.

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